

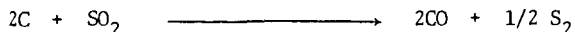
GASIFICATION OF CHAR WITH SULFUR DIOXIDE

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1.0 INTRODUCTION

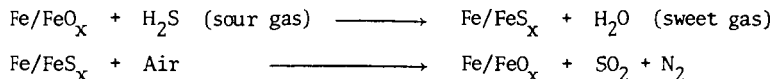
The preliminary experiments summarized here were aimed initially at determining optimum conditions for reducing sulfur dioxide to elemental sulfur with char. However, an important secondary objective followed when we found that carbon monoxide (CO) was the main oxidized product generated in the reduction. In other words, this second objective was focused on the possibility of defining a novel gasification system based on the reaction:



Finally, supporting experiments were made using Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA) to better understand the gasification of char with SO_2 .

2.0 BACKGROUND

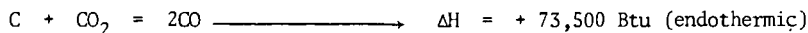
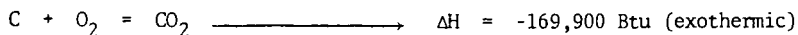
Because of current environmental considerations, many regenerative processes are being proposed to remove sulfur-containing products from the tail gases of coal burning systems. Some of these processes generate a concentrated SO_2 stream at some point. The SO_2 concentration may vary for the particular process; however, it is generally agreed that the most desirable end product is free sulfur. For example, one such process described in two previous papers,^(1,2) is the hot iron/iron oxide desulfurization concept developed by the Babcock and Wilcox Company. Briefly, in this concept, hydrogen sulfide (H_2S) is removed from a fuel gas generated by air-blown suspension gasification of coal. Two overall steps are involved in the desulfurization concept:



After all of the available iron oxide surface scale has reacted to form iron sulfide, regeneration or recovery of the iron oxide is necessary. In practice, this regeneration is accomplished by purging the iron sulfide scale with air to recover iron oxide and a regenerant gas that contains from 10 to 13 vol. percent SO_2 in nitrogen. The overall process concentrates sulfur from less than 1.0 vol. percent in the fuel gas to 10-13 vol. percent SO_2 in the regenerant gas.

In a coal burning process, one readily obtainable reductant is a hot char produced by partial combustion of the coal feed.

The major difference between present-day and earlier coal gasification to medium Btu gas ($CO + H_2$) is the direct use of oxygen in the gasification process. Today, oxygen is used to burn part of the carbon to supply the endothermic heat necessary to drive the gasification reactions. For example, considering coal to be carbon at 1300F, the following reactions occur during oxygen or air gasification:



The sum, $2C + O_2 = 2CO$, $\Delta H = -96,400 \text{ Btu (exothermic)}$, represents overall gasification with oxygen to yield carbon monoxide and recoverable heat.

Depending on the type of gasifier, the upper temperature level during gasification is of prime concern from the standpoint of reaction rates or kinetics. For example, in air-blown entrainment gasification, the short residence time in the high-temperature zone determines gas quality and the fraction of coal gasified.⁽³⁾ In other words, any variable that reduces temperature, such as a heat loss or the presence of steam, detracts from gas quality. Using oxygen instead of air, however, generates such extreme temperatures that some steam addition is necessary to moderate gasification temperature. With steam addition, a second heat consuming reaction occurs, $C + H_2O + CO + H_2$, $\Delta H = +58,500 \text{ Btu (endothermic)}$.

The disadvantage of oxygen-blown gasification relates to the necessity and expense of providing an associated oxygen plant. However, using air as the oxygen source dilutes the gas produced with nitrogen to reduce its heating value to the range of 100 Btu/Scf as opposed to a theoretical 320 Btu/Scf for pure oxygen gasification. Moreover, nitrogen cannot be economically removed from the produced gas.

3.0 POSSIBLE CONCEPT

A second possible route for producing non-nitrogen diluted CO involves the use of SO_2 as the gasification agent. Sulfur dioxide can be separated from N_2 . The following steps might constitute a possible concept for accomplishing this process:

- (1) Sulfur is burned in air to produce a gas containing 19-21% SO_2 .
- (2) Using an acid gas scrubbing system, SO_2 is separated from the inert nitrogen diluent and fed, together with hot char, to a gasifier.
- (3) Undiluted SO_2 reacts with hot char to yield CO and elemental sulfur, $2C + SO_2 \longrightarrow 2CO + 1/2 S_2$.
- (4) Product gases from the gasifier are quenched to separate sulfur from the product CO.

4.0 MAJOR CONCERN

From the standpoint of the basic chemistry involved, the area of greatest concern centers around the calculated endothermic gasification of carbon with SO_2 . For example, the reaction $2C + SO_2 \longrightarrow 2CO + 1/2 S_2$ at 2200F is endothermic to the extent of 880 Btu/lb of SO_2 reduced (50,400 Btu/mole). This calculation is based on the reaction of carbon in the standard state. The carbon in char may, of course, yield slightly different thermodynamics than carbon in the standard state; however, char may contain other constituents like ash that react with SO_2 . These reactions may provide additional heat.

In considering char gasification with SO_2 , one logical question to be addressed is "What differences exist between SO_2 and CO_2 ?" On the surface, CO_2 gasification of carbon is more endothermic to the extent of 1600 Btu/lb of CO_2 reduced (70,400 Btu/mole). Other differences, as we shall see, center around the kinetics or reaction rates involved.

5.0 EQUIPMENT AND PROCEDURE

Basically, two test rigs were used. For the initial tests, a small (1-inch I.D.) externally heated mullite tube served as the reactor sketched in Figure 1. The feed gases ($N_2 + SO_2$) were metered and fed to a preheating section where the gas temperature was increased to about 900F. The hot char temperature was in the range of 1600 to 2000F where reaction occurred. As the products exited the reactor, quenching was accomplished by a device designed to condense sulfur by contact with water in a container filled with glass beads. Product gases were analyzed by gas chromatography.

Later tests were made in a 5-inch diameter tube using a fluidized bed of char. This reactor (sketched in Figure 2) consisted of a 36-inch long silicon carbide tube heated by an outer annular furnace firing natural gas. Bed temperatures of 2200F were easily attained in this furnace. Product gas samples were drawn through a water-cooled stainless-steel probe to quench temperature. As before, gases were analyzed by gas chromatography.

Thermal analysis (DTA and TGA) was performed on an instrument manufactured by Tracor. Kinetic measurements of the carbon, SO_2 , and CO_2 reaction were made at constant temperature with a modified Tracor TGA balance. For the kinetic measurements, a 15 mg sample of graphite was placed in an inert gas while the system was heated to reactant temperature. At the desired temperature, SO_2 or CO_2 was substituted for the inert gas and the weight loss was monitored.

6.0 CARBON SOURCES

Carbon sources were as follows:

- (1) Metallurgical coke (-16 + 30 mesh) with the following analysis:

<u>Proximate Analysis, % of wt.</u>	<u>Ultimate Analysis (Dry), % of wt.</u>
Volatile Matter 0.5	C - 90.8
Fixed Carbon 92.0	H - 0.2
Ash 7.5	S - 0.7
	N - 0.8
	Ash - 7.5

- (2) Coal char from FMC
(3) Pulverized graphite.

7.0 RESULTS

For discussion, the experimental results are broken down into three areas; each area represents a different approach at understanding the gasification step.

1. Bench scale test reactors
2. Differential Thermal Analysis (DTA)
3. Kinetic measurements

7.1 BENCH SCALE TEST REACTOR

Our bench scale test reactors ranged from a small fixed bed to a larger fluidized bed. In the fluidized bed reactor, provision was also made for air addition. The reason of course, for the scale up was to answer questions unanswered by the small reactor.

7.1.1 Fixed Bed Tests

Table 1 illustrates initial test results obtained with the 1-inch I.D. fixed bed reactor. The first two tests illustrated were made with 13 vol. percent SO_2 in nitrogen or a simulated regenerate gas from our hot Fe/FeO_x desulfurization process to determine whether SO_2 could be reduced with hot carbon. The results with both the simulated regenerant gas and pure SO_2 clearly illustrate that carbon was an excellent reductant at temperatures around 2200F and space velocities from 700 to 800. No SO_2 survived the reduction.

The second tests also showed that a significant amount of CO was formed. Unfortunately in the tests with pure SO_2 , a significant amount of COS was produced. We felt that COS probably was formed from the gas phase reaction $\text{CO} + 1/2 \text{S}_2 \rightarrow \text{COS}$ as the gases slowly cooled while exiting the reactor. In other words, it was not possible to reduce temperature rapidly from 2200F in the small reactor.

7.1.2 Fluidized Bed Test

To quench the product gases rapidly, we switched to the water-cooled sample probe and the 5-inch diameter fluidized bed reactor. The objective, of course, was to reduce the time CO and S_2 were in contact with each other at temperatures from 1800F down to the condensation point of sulfur.

Results from the fluidized bed tests with coke were tabulated in Table 2. No SO_2 survived the reduction; all of the SO_2 fed to the char bed was reduced to elemental sulfur or COS. In comparison to the previous tests, quick quenching the product gases reduced the COS level. With simulated regenerant gas (13 vol. percent SO_2) only a trace of COS survived; however, with pure SO_2 the COS level was still quite high or at least 7 vol. percent.

7.1.3 Air Addition

Since the reduction was calculated to be endothermic, several experiments were made to see how much we could back off the external heat and still maintain the SO_2 - char gasification. This was done by decreasing the heat (natural gas) input to the outer annular furnace. Two other changes were made; i.e.,

- (1) Some air was added to the SO_2 but not enough to compensate for the calculated heat uptake of the reaction.
- (2) The bed consisted of coal char instead of metallurgical coke.

Results from part of the tests are found in Table 3. The SO_2 -to-air ratio varied from 2 to 10 vol. SO_2 per vol. of air. Although the tests were not designated to give quantitative information, we were surprised to find that once the reduction started, it maintained itself without the addition of external heat. In other words, the char - SO_2 gasification approached a heat balanced reaction with some air addition.

7.2 DIFFERENTIAL THERMAL ANALYSIS (DTA)

To better define the relative heat uptake of the char/coke reaction with SO_2 and CO_2 , differential thermograms were obtained using the two reactant gases with pulverized metallurgical coke. We found that, because of the highly endothermic fusion of the ash constituents in the coke at 1800 to 2000F, it was necessary to preheat the coke sample blanketed with inert nitrogen to reactant temperature (2350F). Once the prefused ash had been heated and cooled back to ambient temperature, a second heating cycle in inert gas did not reveal the endothermic fusion of the ash. After one cycle in nitrogen, SO_2 or CO_2 was substituted for the DTA measurements. Two typical curves obtained with CO_2 and SO_2 are illustrated in Figure 3. Negative peaks represented endothermic or heat consuming reactions.

Although the differential thermograms were not quantitative, the results (Figure 3) presented a comparative picture of coke gasification with SO_2 and CO_2 . The curves suggested that the CO_2 - coke reaction was far more endothermic at about 2000F where gasification occurs than was the corresponding reaction with SO_2 . In fact, the coke - SO_2 reaction was nearly heat balanced.

7.3 KINETIC MEASUREMENTS

The last series of measurements made involved a comparison of the kinetics, or the rate of weight loss versus time of pulverized graphite in SO_2 and CO_2 . For these measurements, graphite served as the source of carbon instead of metallurgical coke or coal char. The latter sources of carbon proved to be too reactive for accurate kinetic measurements.

For the weight loss-time measurements, a strip chart recorder was added to the basic X-Y recorder in the TGA apparatus to measure sample weight versus time. The weight loss was plotted as a function of time at constant temperature. Figure 4 illustrates a plot of the fractional weight loss versus time curve for graphite gasification with SO_2 at 2100F.

The simplified model used to interpret the weight loss-time curves assumes:

- (a) that the heterogeneous graphite particle mix can be approximated by spheres with an average diameter, initially of r_0 , and at some time later as r . The fractional weight loss, fw , is given by
- (b) that the reaction of carbon is first order with respect to available carbon atoms; and
- (c) that the concentration of SO_2 or CO_2 in a flowing system is constant,

$$fw = 1 - \frac{r^3}{r_0^3}; \quad (1)$$

$$\frac{dc}{dt} = -k Ca, \quad (2)$$

where (dc/dt) represents the rate of carbon atom gasification and 'Ca' is the concentration of available carbon atoms on the surface of the graphite particle being gasified. The rate of decrease of the particle radius is constant, or

$$\frac{dr}{dt} = -k' \quad (3)$$

Differentiating equation (1), substituting for 'r' and integrating gives the following expression that relates the fraction reacted (fw) to time (t) by the temperature function of the reaction (k').

$$1 - (1-fw)^{1/3} = k't \quad (4)$$

The use of equation (4) to fit the experimental data is illustrated in Figure 4 by the dashed line. Similar fits are obtained for the other experimental weight loss-time curves.

The spherical model represents only a crude approach at defining the temperature function of the reaction. The Arrhenius expression for the rate constant k' is:

$$k' = Ae^{-E/RT} \quad (5)$$

The utility, however, of the simplified approach is that it gives us a means of estimating the temperature-time performance of graphite gasification with SO₂ or CO₂.

From the rate constants, Figure 5 was constructed. These curves represented the time-temperature relationship to gasify 50, 75, and 90 wt. percent of graphite with SO₂ and CO₂. Several points were indicated:

1. The rate of gasification is faster at a given temperature with SO₂ than CO₂. For example, the time required to gasify 50 wt. percent of the graphite at 2300F ranges from 15 minutes for SO₂ to 60 minutes for CO₂ (no thermodynamic limitation at 2300F).
2. The predicted rates apply only for pulverized graphite. Char gasification would give a more rapid rate because of a higher specific surface area.
3. A few seconds at 3000F is worth tens of minutes at lower temperatures for equivalent gasification.

8.0 CONCLUSIONS

From this process oriented study, our conclusions are as follows:

- (1) SO₂ in a nitrogen containing regenerant gas can be converted primarily to CO and sulfur by reaction with carbon (char) at temperatures in excess of 2000F.
- (2) The gasification of char with SO₂ may proceed along several paths. Some of these may be exothermic such that the overall reaction is nearly heat balanced.
- (3) The burning of sulfur in an air atmosphere and the subsequent separation to produce a highly concentrated SO₂ gas may prove to be an economical means of producing a high CO content gas without requiring an oxygen plant.
- (4) SO₂ gasification of carbon proceeds at a faster rate at a given temperature than the CO₂-carbon reaction.

In terms of our initial objectives, SO_2 can be completely reduced to elemental sulfur by reaction with hot char. Further, aside from free sulfur, CO is the primary product formed from the reduction.

REFERENCES

1. Bhada, R.K. and Sage, W.L., Preprints, Div. of Fuel Chemistry, A.C.S., 14, No. 4, (101) 1970.
2. Kertamus, N.J., *ibid*, 18, No. 2 (131) 1973.
3. Sage, W.L., *ibid*, (211).

TABLE 1 FIXED BED (COKE)

Input Gas Flow Ft ³ /hr	GHSV*	Input% SO ₂	Avg. Temp. °F	%CO ₂	Output %N ₂	%CO	%COS	Test Length Min.
6.80	773	13	2230	5	77	18	-----	60
4.384	813	100	2100	32.5	---	43.0	24.5	30
4.384	776	100	2220	11.0	---	42.0	47.0	60

Ft³ of gas/hr @60F

*Gaseous hourly space velocity =

Ft³ of bed (initial)

TABLE 2 FLUIDIZED BED (COKE)

Input Gas Flow Ft ³ /min	GHSV	Input% SO ₂	N ₂	Avg. Temp. °F	%CO ₂	Output %N ₂	%CO	%COS	Test Length Min.
0.56	1.93	100	--	2240 -	< 1	4	80	7	15
0.9	391	100	--	2100	< 1	5	76	7	35
				2250					
0.9	315	100	--	2250	6	1	68	22	25
1.9	813	13	87	2000 -	< 1	80	18	1	60
				2100					

TABLE 3 AIR ADDITION TO SO₂ (CHAR)

Input Gas Flow Ft ³ /min	GHSV	Input SO ₂	Gas% N ₂	% O ₂	Avg. Temp. °F	CO ₂	Output N ₂	Gas% CO	COS	Test Length Min.
1.13	276	13	87	----	1800	1	69	24	2.7	85
1.1	264	14.2	84.9	.903	1900	< 1	84	17	1	250
0.683	252	15.6	83.5	.945	2060	< 1	62	35	2.0	300
0.379	138	89.2	8.5	2.3	2210	< 1	3.7	87.0	9.2	153
0.45	164	100	----	----	2240	11.6	---	79.7	8.6	153

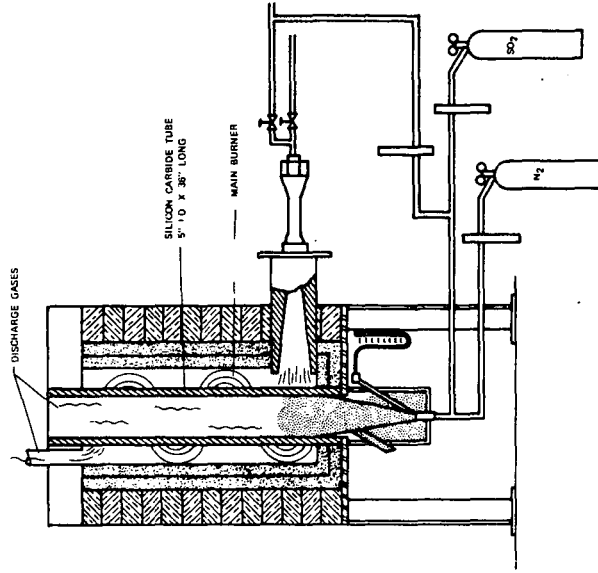


FIGURE 2. 5-INCH FLUIDIZED BED REACTOR

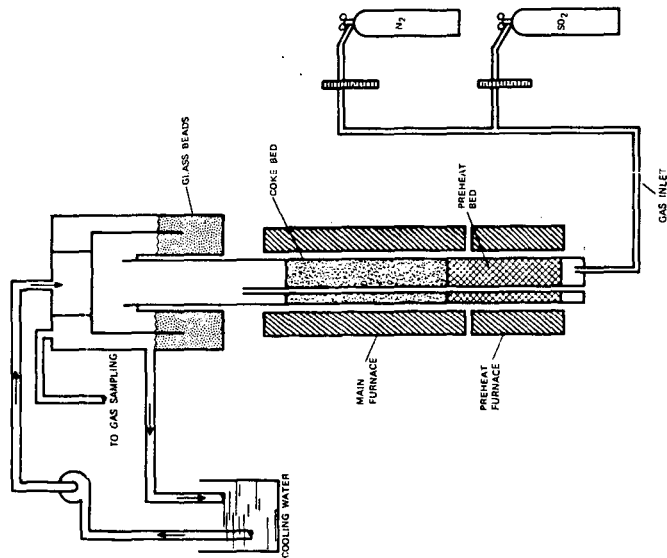


FIGURE 1. FIXED BED GASIFIER

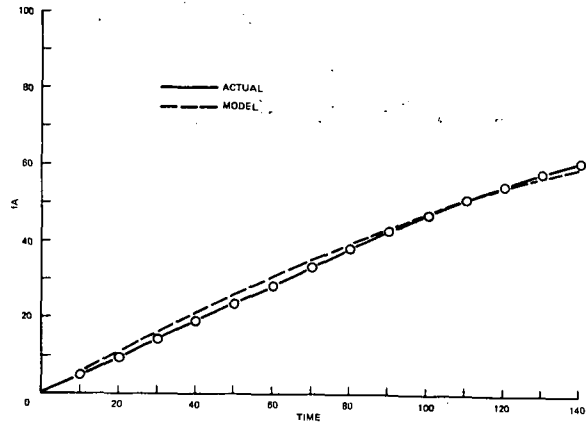
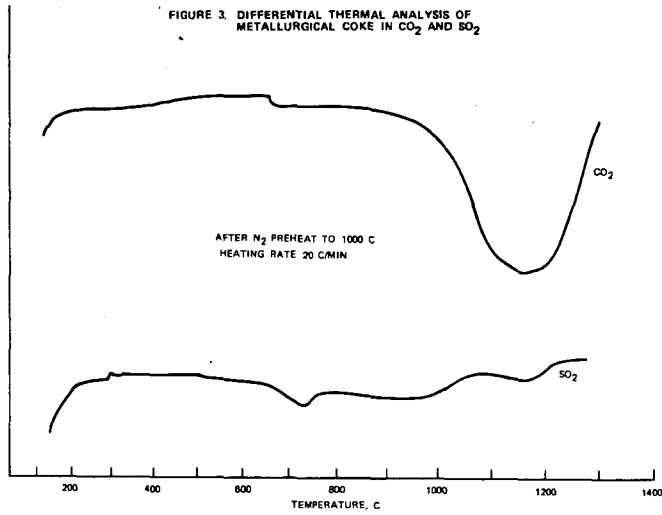


FIGURE 4. FRACTIONAL WEIGHT LOSS VS. TIME
GRAPHITE + SO_2 AT 2100 F

FIGURE 5. GASIFICATION OF GRAPHITE

